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(54) Title: ALKALINE CELL HAVING A CATHODE INCORPORATING EXPANDED GRAPHITE		
(57) Abstract An electrochemical cell has a cathode containing an expanded graphite as an electrically conductive carbon material. The expanded graphite has a kerosene absorption in the range of 2.2 to 3.5 ml/g, to provide enhanced service performance to the cell.		

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ALKALINE CELL HAVING A CATHODE INCORPORATING EXPANDED GRAPHITE

5 The present invention relates to electrochemical cells, particularly alkaline electrochemical cells, having cathodes formed of a mixture of manganese dioxide together with a conductive carbon material for forming a conductive matrix.

 Typical alkaline electrochemical cells have a cylindrical steel can, with a cathode
10 containing manganese dioxide as active material formed on the interior surface of the steel can. An anode having zinc powder and binding agent is dispensed in the central portion of the cell. A separator is located between the anode and the cathode, and an alkaline electrolyte contacts the anode, cathode, and separator. A conductive anode current collector is generally inserted in the anode active material, and a cover and seal assembly
15 closes the open end of the steel can.

 In conventional alkaline cells, the cathode is configured as the positive electrode, while the anode is configured as the negative electrode. The cathode typically comprises a mixture of electrolytic manganese dioxide particles as the cathode active material, graphite
20 as the electroconductive material, potassium hydroxide solution, and deionised water. The conductive graphite is added to enhance the electrical conductivity between the manganese dioxide particles and also to enhance electrical conductivity between the steel can and the cathode active material, as the manganese dioxide has an extremely low specific conductivity. As a consequence, the conductive graphite provides an electroconductive
25 matrix throughout the active manganese dioxide particles as well as with the steel can.

A primary goal in designing alkaline cells is to increase the service performance of the cell. The service performance is the length of time taken for the cell to discharge, under a given load, to a specified voltage at which the cell is no longer considered useful for its intended purpose. One approach taken to increase service performance has been to increase the internal volume of the cell, in order to increase the amount of active materials that may be employed within the cell. However, the external size of the cell is generally fixed by commercial constraints, thereby limiting the ability to increase the amount of active materials within a particular size cell.

10 Within the cell, a higher content of graphite mixed with cathode active material can enhance the electrically conductive properties of the cathode. However, a larger amount of graphite necessarily also consumes a larger volume which, in turn, causes a reduction in the amount of the manganese dioxide active material that can be used in the cathode, thereby leading to a reduction in the discharge capacity of the battery. On the other hand, a decrease in the amount of graphite allows an increase in the amount of active manganese dioxide that can be used, but can lead to an increase in the internal resistance of the cathode, thereby decreasing the cell's discharge performance. Accordingly, it is necessary to achieve a suitable compromise between the proportion of conductive material and manganese dioxide active material contained within the cathode of the cell.

20

Various attempts have been made to improve the discharge characteristics of electrochemical cells, particularly at high discharge rates. Since the conductivity of manganese dioxide is relatively low, auxiliary conductive agents, such as graphite and/or acetylene black, are frequently mixed in with the other cathode components. However,

graphite and acetylene black have intrinsic drawbacks, including large consumption of volume and high absorption characteristics.

In addition, conventional conductive additives employed in the cathode of the cell
5 include high levels of impurities, leading to increased gassing. Excessive gassing of hydrogen is well known to decrease the performance of the cell. Accordingly, it is desirable to minimise the amount of gassing in the cell. Despite past increases in service performance with such additives, the need to find new ways to increase service performance remains the primary goal of cell designers.

10

Expanded graphite having an average particle size of 0.5 to 15 μm has been disclosed in US-A-5,482,798 as being advantageously incorporated into alkaline cells having a manganese dioxide cathode.

15 It has now, surprisingly, been found that the service performance of alkaline electrochemical cells can be improved by the incorporation of a conductive, expanded graphite particulate material having certain characteristics into the cell's cathode.

Thus, in a first aspect, the present invention provides an electrochemical cell
20 comprising a positive electrode having an active material and an electrically conductive carbon material including expanded graphite particles, characterised in that the expanded carbon particles have a kerosene absorption value in the range of 2.2 to 3.5 ml/g.

More generally, there is provided a cathode for an electrochemical cell comprising an active cathode material, such as electrolytic manganese dioxide, combined with an electrically conductive carbon, comprising expanded graphite particles, for providing a conductive matrix which occupies low volume, the expanded graphite particles preferably having a kerosene absorption in the range of 2.2 to 3.5 ml/g. The cathode of the present invention is particularly adapted for use in electrochemical cells having an alkaline electrolyte.

In an alternative aspect, the present invention provides an electrochemical cell comprising a positive electrode having an active material and an electroconductive carbon material including expanded graphite particles having a purity level of greater than 99.9%, preferably greater than 99.95%, as determined by weight loss on ignition.

The cathode of the electrochemical cell according to one aspect of the present invention includes an active cathode material, such as electrolytic manganese dioxide, combined with an electrically conductive carbon comprising expanded graphite particles for providing a conductive matrix occupying a low volume. The expanded graphite particles preferably have an average surface area-to-mass ratio of at least $18 \text{ m}^2/\text{g}$, an average particle size in the range of 17 to 32 μm , and a kerosene absorption in the range of 2.2 to 3.5 ml/g. The cathode of the present invention is particularly adapted for use in electrochemical cells having an alkaline electrolyte.

The cells of the present invention employ expanded graphite having certain characteristics. Essentially, the graphite is expanded and graded in order to achieve a

desired end result, which appears to be characterised by a cup-shaped, rather than flat, particle. Such particles seem better able to contact the manganese dioxide of the electrode, thereby providing better conductivity which, accordingly, allows the amount of graphite required to be reduced. The resulting volume can then be occupied by active material
5 instead, thereby increasing performance and service life.

The graphite of the present invention has certain physical characteristics. Provided that certain characteristics are present, then the graphite is useful. These characteristics do not necessarily define the graphite, but are properties thereof. In particular, the kerosene
10 absorption test has not previously been applied to graphite, but it has now been found that suitable graphite generally has a kerosene absorption of 2.2 to 3.5 ml/g.

Other characteristics which may be used to characterise the graphite, either individually, or in any combination, are, in generally descending order of importance:
15 average particle size (d_{50}); d_{90} particle size; surface area to mass ratio (BET specific surface area); tap density; and Scott density. The d_{10} particle value is also a useful measurement, especially in combination with the d_{50} and/or d_{90} measurements.

The present invention will now be further illustrated with respect to the
20 accompanying drawings, in which:

Figure 1 is a cut-away perspective view of one example of an alkaline electrochemical cell constructed in accordance with the present invention;

Figure 2 is a flow diagram illustrating a method of producing expanded graphite for use in a cathode of an electrochemical cell;

Figure 3 is an enlarged photographic view of expanded graphite additive for use in a
5 cathode of the electrochemical cell;

Figure 4 is a table illustrating the performance analysis of various samples of tested expanded graphite and measured characteristics thereof;

10 Figure 5 is a graph illustrating the mean diameter of volume for the tested expanded graphite particles as provided in Figure 4;

Figure 6 is a graph illustrating the mean diameter of area for the tested expanded graphite particles as provided in Figure 4;

15

Figure 7 is a graph illustrating the expanded graphite's kerosene absorption for the tested expanded graphite samples as provided in Figure 4;

Figure 8 is a graph illustrating the Scott volume of the tested expanded graphite samples as
20 provided in Figure 4;

Figure 9 is a graph illustrating the expanded graphite's BET surface area for the tested expanded graphite samples as provided in Figure 4;

Figure 10 is a graph illustrating pellet resistance for the tested expanded graphite samples as provided in Figure 4;

Figure 11 is a block diagram illustrating the methodology for determining a preferred
5 expanded graphite for use in a cathode of an electrochemical cell according to the present invention; and

Figure 12 is a graph illustrating tap density measured for samples of expanded graphite particles.

10

Referring now to Figure 1, a cut-away view of a cylindrical alkaline electro-chemical cell 10 is shown. Alkaline cell 10 includes a steel can 12 having a cylindrical shape and one open end. A metallised, plastic film label 14 is formed about the exterior surface of steel can 12 except for the ends of steel can 12. At the closed end of steel can
15 12 is a positive cover 16 preferably formed of plated steel. Film label 14 is formed over the peripheral edge of positive cover 16.

A cathode 20, preferably formed of a mixture of manganese dioxide, graphite, 45% potassium hydroxide (KOH) solution, deionised water, and a conductive can coating, is
20 formed about the interior side surface of the steel can 12. Additionally, an optional binder may be added to the cathode mixture 20. A separator 22, which is preferably formed of a non-woven fabric that prevents migration of any solid particles in the cell, as well as providing electrical insulation, is disposed about the interior surface of cathode 20. An electrolyte 24 formed of potassium hydroxide is disposed within the interior of the

separator 22. An anode 18, preferably formed of zinc powder, a gelling agent, and other additives, is disposed within the electrolyte 24 in contact with a current collector 26, which may be formed of brass. Accordingly, the cathode 20 is configured as the cell's positive electrode, and the anode 18 is configured as the cell's negative electrode.

5

Current collector 26 contacts the negative cover 36. A nylon seal 30 is formed at the open end of steel can 12 to prevent leakage of the active ingredients contained in the steel can 12. A negative cover 36, which is preferably formed of plated steel, is disposed in contact with the current collector 26. The negative cover 36 is electrically insulated
10 from the steel can 12 by the nylon seal 30.

The cathode 20 of the present invention contains an active cathode material, such as electrolytic manganese dioxide (EMD). In addition, the cathode 20 further contains a conductive carbon material, referred to herein as expanded graphite, to provide a
15 conductive matrix within the cathode 20 between the manganese dioxide particles as well as between the manganese dioxide and the steel can to provide for enhanced service performance of the electrochemical cell 10.

The cathode 20 of the present invention preferably employs electrolytic manganese
20 dioxide (EMD) particles as the active cathode material. Electrolytic manganese dioxide has a relatively low specific conductivity and, therefore, a conductive material is typically added with the electrolytic manganese dioxide particles to the cathode 20. In accordance with the present invention, a conductive material is added to the electrolytic manganese dioxide in an amount that allows for lower cathode resistance and which enhances the

electrical conductivity within the cathode 20, and allows for a greater amount of manganese dioxide which increases the service performance of the cell.

According to the present invention, expanded graphite particles are added to the cathode 20 as conductive material. As used herein, expanded graphite is graphite in which the crystal lattice has been expanded. There are many known methods for expanding graphite, including, for example, incorporation of acid/oxidant, followed by thermal treatment.

Expanded graphite can be added as the electrically conductive material in an amount less than that normally required for conventional graphite, but which yet provides adequate conductivity and cathode mouldability, thereby increasing overall cell performance, especially under high discharge rate applications. The use of expanded graphite in the alkaline cell cathode 20 provides a much lower overall bulk cathode resistivity as compared to conventional carbon which includes a crystalline graphite. Expanded graphite further allows for the use of a greater amount of electrolytic manganese dioxide within the generally predefined volume of the cathode 20 of the alkaline cell 10.

Referring, now, to Figure 2, a method 40 of manufacturing and using expanded graphite in the cathode 20 of cell 10 is shown. The expanded graphite additive, according to one embodiment, preferably includes a natural graphite that is first chemically treated and then heated so that it expands in size as described by the following process.

A natural graphite, which is typically mined from the earth pursuant to step 42, is purified to a high purity level in step 44. The purification process may include a thermal treatment process as disclosed in US-A-3,807,961 (Markel), or by other techniques, such as successive flotations and chemical treatment. In step 46, the high purity graphite is preferably soaked in sulphuric acid and nitric acid until each of its graphite layers have been acid soaked therein. Alternatively, hydrogen peroxide and chromic acid may be used in the acid treatment of the graphite.

Once the graphite layers have been acid soaked, preferably by vacuum impregnation, the graphite is ready for heat treatment, as provided in step 48. The degree of expansion of the graphite layers may be controlled by careful time and temperature control. The heating process preferably involves quickly placing the acid-treated graphite material into a furnace at approximately 1000°C for an approximate time period of two to ten minutes, until the graphite expands in size and de-laminates. An oven temperature in the range of 850°C to 1100°C is suitable for the heat treatment. This heat treatment process expands the graphite to approximately three hundred times its original thickness and provides a wrinkled, wavy surface. The resulting expanded graphite layers are typically much thinner than the conventional, non-expanded, crystalline graphite layers.

Following the heating process in methodology 40, the expanded graphite is compacted, as provided in step 50. The compacted expanded graphite may also be washed and dried at this point. Next, the compacted expanded graphite undergoes a milling process, using a jet mill. It is preferred that the milled expanded graphite has an average particle size in the range of seventeen to thirty-two μm (17-32 μm), as provided in step 52.

As used herein, the average particle size is referred to as the d_{50} mean average particle size, which can be measured with a Microtrac full range analyser. The particle size below which 90% of the total distribution lies is referred to as the d_{90} value, and the particle size below which 10% of the total distribution lies is referred to as the d_{10} value. When the
5 milling process is complete, the expanded graphite may then be premixed with manganese dioxide and other additives to form the cathode 20 of cell 10, as provided in step 54. The cathode mix is preferably disposed in the steel can of cell 10, and cell 10 is preferably assembled according to known impact or ring moulding techniques.

10 According to the cathode impact moulding cell assembly technique, method 40 proceeds to step 55, in which the cathode mix is added to the can. The cathode mix is then impact moulded via step 56 in accordance with known impact moulding techniques. This generally includes packing the cathode mix with the use of a cylindrical ram rod forcibly actuated through the longitudinal axis of the can. This may include either adding the entire
15 mix and subsequently impacting the cathode mix with the ram rod, or sequentially adding some mix and thereafter packing with the ram rod. In any event, the ram rod forms an anode cavity centrally located within the cathode mix.

According to a cathode ring moulding technique, method 40 proceeds to step 57 in
20 which the cathode mix is moulded into rings. The process of forming ring moulded cathodes generally includes adding a measured charge of cathode mix to a ring-shaped die set and, with the use of a die press, moulding the cathode mix into the shape of a ring. The process of forming and inserting moulded cathode rings into a cell can is widely known in the art. Next, according to step 58, one or more ring moulded cathode rings are inserted

into the steel can. This may be accomplished by loading a fixed number of one or more cathode rings onto a mandrel, which is then lowered into the can and the cathode rings are pressed into the can by way of an upper punch. The number of cathode rings inserted into a particular cell may vary depending on the size of the cell. For example, for AAA- and
5 AAAA-type alkaline cells, three or four cathode moulded rings may be adequate to form the cathode of each cell. Once inserted, the cathode rings are compressed together in step 59, so that the rings are compactly fit, stacked one on top of the other, and located about the inner wall of the can.

10 For the purposes of illustration, a process of producing an expanded, highly lamellar graphite product for use in the present invention is described in more detail as follows. The process requires the provision of a suitable starting material of lamellar graphite; the intercalation of the starting material with a graphite intercalation compound (GIC); the expansion of the GIC to obtain thermally expanded graphite; and air milling the thermally
15 expanded graphite to obtain a de-laminated, exfoliated graphite product having a high degree of uniformity in particle size, a high bulk volume, and a high surface area to mass ratio.

The starting material is preferably natural mineral flake graphite or synthetic graphite having a degree of three dimensional ordering, *i.e.*, highly oriented pyrolytic graphite
20 ("HOPG"). The degree of three dimensional ordering of the graphite can be quantified by x-ray diffraction ("XRD"). The XRD parameter generally used is referred to as L_a and, based on XRD analysis, the graphite best suited for the inventive process has L_a values in excess of 2.000 Å (0.2000 nm) and preferably higher.

In a preferred method, the starting material is natural flake graphite, generally as mined in Mozambique, that is processed to a minimum level of purity of 99.9 LOI (loss on ignition), with the particle size of the graphite being between about -20 mesh and +60 mesh and, preferably between about 30 mesh and 70 mesh (200 - 600 μ m). Such a natural flake
5 graphite can be obtained from the Superior Graphite Co. of Chicago, Illinois, as 2901 grade graphite.

The purified starting material is then intercalated with a GIC that will insert between the lamellae of the graphite structure. There are many different methods by which this can
10 be accomplished. Typically, the graphite particles are treated with a strong oxidising acid, such as highly concentrated combinations of sulphuric and nitric acid. If sulphuric acid is used as an intercalating acid, the sulphur content of the acid treated graphite should be at least 2.0% by weight, and preferably as high as 3.0%. A preferred intercalated graphite is acid-treated chemical flake graphite from UCAR Carbon Company of Danbury, Connecticut,
15 which is natural graphite intercalated with sulphuric acid and nitric acid. The volatile content of the preferred flake graphite after intercalation is preferably between about 12% to 22% by weight.

Next, the intercalated graphite is treated to cause the formation of the GIC, forcing
20 the lamellae of the individual particles to separate and, thus, expand the graphite to an accordion-like configuration. If the graphite is acid intercalated, the expansion is accomplished by rapidly heating the intercalated graphite to temperatures of about 850°C to 1,000°C. Such heating may be done any number of ways, such as by directly heating the intercalated graphite with a flame, by placing the intercalated graphite on a hot surface, by

using infra-red heating elements, by inductive heating, or the like. The intercalated graphite is thermally expanded to produce a product that is typically expanded to greater than 125 times its initial volume, with a bulk volume of approximately 250 ml/g or more and with a surface area-to-mass ratio of 35 m²/g or greater.

5

After the graphite has been suitably intercalated and exfoliated, the graphite is subjected to air milling, which further de-laminates and separates the expanded graphite. This yields a fine graphite that exhibits a substantially higher specific surface area than the same material milled to the same particle size, but not intercalated and expanded. The expanded graphite is milled in a fluid energy-type attrition mill, or air mill. In the preferred process, a flat-configured or "pancake-type" air mill is used to produce a product that may have a mean particle size of approximately 30 μ m and a surface area-to-mass of greater than 18 m²/g.

10

15

The expansion or exfoliation and milling steps for producing expanded graphite may include the following. The intercalated graphite flakes (preferably the flake graphite identified above) is dumped into a flake feeder, from which the graphite flake is fed continuously into the flame of a gas-fire calciner/furnace to cause the intercalated flake to be heated to temperatures of at least approximately 870°C (1,600°F) in less than one minute. In practice, the intercalated graphite flakes are fed into the calciner at a rate of approximately 150 lb/hr (68 kg/hr).

20

In the calciner, the intercalated graphite flake is preferably expanded to form thermally expanded graphite flakes or worms having a bulk volume of at least 250 ml/g and

a surface area-to-mass ratio of approximately $35 \text{ m}^2/\text{g}$. The thermally expanded graphite worms exit the calciner and enter a cyclone which separates the thermally expanded graphite flake from the entraining burner gases. The thermally expanded graphite flakes drop out of the bottom of the cyclone into a second flake feeder, while the exhaust gases from the
5 calciner exit the top of the cyclone to a scrubber.

From the flake feeder, thermally expanded graphite flakes are fed to an air mill. The air mill includes a positive feed induction system, a grinding and classifying ("reduction") chamber, and a single discharge. The thermally expanded graphite flake entering the
10 reduction chamber is entrained by a stream of circulating fluid (air), and jet action breaks up the thermally expanded graphite particles by inter-particle collisions. The centrifugal force shifts the larger, heavier thermally expanded graphite flakes toward the outer periphery of the reduction chamber, causing them to be re-introduced into the jet stream for further grinding. The finer particles migrate towards the outlet of the mill.

15

In practice, the air mill is an Aljet 24 inch (610 mm) flat-configured attrition mill, which processes the thermally expanded graphite flake at a rate of approximately 120 lb/hr (54 kg/hr) to produce a thermally expanded graphite flake having a bulk volume of approximately 0.050 g/cc (or 200 ml/g), a surface area-to-mass ratio of at least about 18-22
20 m^2/g , and a mean particle size of approximately 30 μm . These characteristics for the air milled thermally expanded graphite flake can be varied by adjusting the rate at which the thermally expanded graphite flake is milled. Overfeeding the mill results in coarser thermally expanded graphite flakes, while underfeeding results in finer thermally expanded graphite flakes.

The air milled thermally expanded graphite flakes pass through a second cyclone, which separates out the milled thermally expanded graphite flakes of the desired mass and deposits them into a finished product bin. The undersized thermally expanded graphite flakes or "fines" are exhausted from the cyclone into a bag house, from which the fines are deposited into a "waste" bin. The desired expanded graphite particles are then employed in the cathode of cells according to the present invention.

One of the main features of the expanded graphite of the present invention is its particle shape, which allows for achievement of a low-weight percent carbon containing alkaline cell cathode. Referring, now, to Figure 3, a photograph taken with a scanning electron microscope (SEM), magnified at a power of 5000 x, there is illustrated expanded graphite manufactured according to the aforementioned process. The expanded graphite crystals have a cupped or baseball-glove shaped configuration. This is in contrast to conventional crystalline graphite, which typically has a flatter, laminar surface.

It is believed that the cupped-shaped configuration has the advantage of allowing the expanded graphite particles to have more contact points with the electrolytic manganese dioxide particles than conventional flat graphite and, thus, expanded graphite particles provide a lower, overall contact resistance, whereas a flat crystalline graphite would, theoretically, have only one contact point on its surface with an electrolytic manganese dioxide particle.

The multiple contact points provided with the expanded graphite particles allow enhanced electrical contact and, therefore, allow for a reduction in the amount of graphite that is required in the cathode 20 of cell 10. The multiple contact points which are realised with the expanded graphite particles allow a greater number of conductive paths between
5 manganese dioxide particles so that alternative electrically conductive paths are made available. This can be especially advantageous should oxidation or electrical discontinuity develop in one or more current paths. In addition, the expanded graphite particles may provide enhanced electrolyte retention.

10 Once formed and milled, the expanded graphite particles can be mixed with the electrolytic manganese dioxide to form the cathode 20, as follows. The expanded graphite may be used to form cathode mixes with different conductivities based on the electrolytic manganese dioxide used, as one manganese dioxide may provide a better fit with a cup-shaped expanded graphite particles than others, particularly based on particle shape and
15 size of the expanded graphite. Such parameters can be optimised as necessary.

The electrolytic manganese dioxide and cup-shaped expanded graphite particles are mixed together in a mixer for a short time at a high intensity. The mixer may be an FS Series Model No. LFS-GS-2J, manufactured and sold by the Fukae Powtec Corp. of Japan,
20 having a blender with a vertically oriented agitator blade that pushes the material to the sides of a specially shaped drum. On the side of the drum of the mixer is a small, high-speed chopper blade that performs the actual mixing. The design of the drum affords even blending of all portions of the added powder. It is recommended that the electrolytic manganese dioxide and expanded graphite particles be mixed for a period of three to seven

minutes at a speed of 250-1000 RPM with an agitator blade and at a speed of 680-2500 RPM with a chopper blade. Extended mixing may result in finely ground expanded graphite particles and increased electrical resistivity.

5 According to the aforementioned mixing technique, a specific sequence is preferably followed. The heaviest material, particularly the electrolytic manganese dioxide, is first added to the mixer, followed by the lighter materials, such as the expanded graphite particles. When properly mixed, the electrolytic manganese dioxide and expanded graphite materials should not separate during subsequent handling.

10

 According to one embodiment, the cell's bulk cathode preferably contains an amount of expanded graphite in the range of 3.2% to 6.25% by weight of the total cathode, and more particularly contains expanded graphite of approximately 5% by weight of the total cathode. This is in contrast to conventional cells which commonly require
15 conventional synthetic graphite in an amount of 8% to 10.5% by weight of the total cathode for the same cathode size and configuration. Accordingly, the use of expanded graphite consumes less volume and weight than conventional graphite currently used in alkaline cells. As a consequence of using a conductive material of less volume, additional volume remains available in the cathode to employ added electrolytic manganese dioxide
20 or other active cathode materials, thereby leading to enhanced service performance of the cell, particularly for high-rate service applications.

 With particular reference to Figure 4, measured results for flooded half-cell testing for various expanded graphite materials are shown. The half-cell configuration involves

the testing of a 0.5 gram cathode pellet in a flooded electrolyte condition. A 100 mA/g electrolytic manganese dioxide discharge corresponds to approximately 1000 mA constant current discharge for a current standard size AA electrochemical cell. A 20 : 1 weight ratio of electrolytic manganese dioxide : carbon in the cathode mixture was used,
5 corresponding to 4.8% by weight of carbon in the mix.

In all, the expanded graphite of the present invention exhibited a d_{50} average particle size of approximately 23.6 μm when measured with the Microtrac full range analyser. The Microtrac full range analyser reading provides a d_{50} average particle size
10 and d_{90} and d_{10} values. A suitable Microtrac full range analyser is the Model No. 9200 Series, manufactured and sold by Microtrac, Inc. The Microtrac full range analyser also initially calculates the area and perimeter of the measured particles, from which a volume can be calculated. The Microtrac full range analyser further determines a mean average volume and mean average area of the measured particles. According to the present
15 invention, it is preferred that a d_{50} average particle size be in the range of 17 to 32 μm , as measured with the Microtrac full range analyser.

As shown in FIG. 4, a plurality of samples of expanded graphite, labelled samples S1 through S17, was analysed as to performance and physical characteristics. For each
20 sample of expanded graphite, a service time was measured in minutes to reach a 0.9-volt cut-off, in accordance with a 100 mA/g electrolytic manganese dioxide discharge for the flooded half-cell test. Sample S1 achieved the highest service performance of 97.1 minutes. In addition to service performance, the average particle size (d_{50}), d_{90} value and d_{10} value (in micrometers), as measured with the Microtrac full range analyser, are

provided, along with the calculated mean diameter of volume and mean diameter of area, as calculated by the Microtrac full range analyser.

Other performance measurements include BET surface area (m^2/g), kerosene
5 absorption (ml/g), pellet resistance (ohms), water (weight percent), Scott density (g/cm^3),
and real density (g/cm^3). Additional measurements include calculated surface area
(m^2/cm^3), bulk volume (g/cm^3) and tap density (g/cm^3) measurements. Optimum service
performance was achieved with sample S1 with a service performance time of 97.1
minutes for an expanded graphite having an average particle size of 19.61 micrometers.
10 However, service performance may differ depending on the various characteristics of the
expanded graphite, as well as the manganese dioxide and other characteristics of the cell.

Referring to Figures 5-10, selected measured test data, which are shown in the
table of Figure 4, are shown plotted in graphs and can be used to determine an optimum
15 expanded graphite for use in a cathode of a cell. In particular, Figure 5 illustrates the mean
diameter of volume versus service performance time in minutes for each of the samples
S1-S17 of expanded graphite, as measured with the Microtrac full range analyser. Figure 6
illustrates the mean diameter of area, as measured with the Microtrac full range analyser
along with the service performance time in minutes. Figure 7 illustrates the kerosene
20 absorption of the expanded graphite in millilitres per gram (ml/g) versus the service
performance time. Figure 8 illustrates a measurement of the Scott volume in grams per
cubic inch (g/in^3) versus the service performance time. Figure 9 illustrates the expanded
graphite BET surface area in meters squared per gram (m^2/g) versus the service

performance time, while Figure 10 illustrates the cathode pellet resistance in ohms versus the service performance time.

From each of the graphs provided in Figures 5-10, determinations can be made as
5 to the optimum expanded graphite that may be used for a given cathode in a cell to achieve optimum service performance for an intended application.

The physical characteristics of the expanded graphite particles can be measured with the Microtrac full range analyser or other comparable particle analyser. Physical
10 characteristics of expanded graphite particles that can be measured with such a particle analyser include the mean diameter of volume, mean diameter of area and a calculated surface area.

Kerosene absorption is an indication of the ability of the expanded graphite to
15 absorb electrolyte, relative to kerosene. The expanded graphite of the present invention has a preferred kerosene absorption in the range of 2.2 to 3.5 millilitres per gram (ml/g), more preferably 2.6 to 3.3 millilitres per gram (ml/g), and most preferably in the range of 2.7 to 3.1 millilitres per gram (ml/g). Kerosene absorption measurements can be provided by wetting a fixed amount of expanded graphite with kerosene/surfactant solution made up
20 of 96% kerosene and 4% dimethyl di(cocoalkyl) quaternary ammonium chlorides, one example of which is commercially available as ARQUAD 2C-75 from Akzo Nobel Chemicals, Inc. The kerosene is added at a fixed rate, with continuous agitation, until expanded graphite agglomerates join and become a single ball, at which time an absorption value is determined by the number of millilitres of test solution added to the sample.

In a specific embodiment, the kerosene absorption test procedure includes adding 10 to 25 grams, plus or minus 0.1 gram, of a sample of expanded graphite to a clean, dry 500 millilitre Erlenmeyer flask, and inserting the flask in a holder of a shaking machine.

5 The tip of a burette is adjusted to a preferred height of about one inch above the mouth of the flask. The shaker may be a Burrell wrist action shaker Model No. BB, made available by Burrell Scientific, or equivalent, with the amplitude lever set to position "5" to produce a mild agitation of a sample in the flask. A stopcock on the burette is opened and the kerosene solution is dispensed at the rate of three to four drops per second, which
10 corresponds to approximately nine to twelve millilitres per second. As the solution is added and the mixture becomes agitated, a point will be reached where the powdered material forms small agglomerates. At this point, the amplitude of the lever of the shaker is preferably raised to position "10" and, also, the solution being added should be reduced to one drop per second, to avoid passing the end point. As the solution is added and the
15 shaking continues, small balls combine with one another to produce larger balls and, as the end point approaches, a desired single ball is realised. When a single ball that does not break down with continued shaking is formed, the burette reading is recorded and the absorption value is equal to the number of millilitres of test solution added to the sample.

20 In addition, other measured test data may include a tap density value of the expanded graphite. The tap density testing procedure includes subjecting a fixed sample weight of expanded graphite to a predetermined number of taps, such as 1,000 taps, at a first frequency over a period of time, such as four minutes, in a graduated cylinder to achieve packing, *e.g.*, filling in of voids, in a consistent and repeatable manner.

The procedure includes weighing the predetermined amount of expanded graphite in a graduated cylinder using a powder funnel. The cylinder may be placed in a dual auto tap device such as Model No. DA1, made available from the Quantachrome Corporation.

- 5 The dual auto tap device is set to provide uniform repeated taps to the cylinder for the predetermined period of time to provide a predetermined number of taps. The cylinder is then removed from the apparatus and the volume of the sample of expanded graphite is measured. In addition, the expanded graphite is weighed. The tap density value is a function of the measured weight in grams of expanded graphite divided by the measured
- 10 volume following the tap density testing procedure. This tap density testing procedure provides for a tap density value in grams per cubic centimetres (g/cc).

- Referring particularly to Figure 12, the graph provides an illustration of measured tap density values as determined in accordance with the aforementioned tap density testing
- 15 procedure. The tap density is provided as a function of the service performance time and minutes for each of the samples of expanded graphite to reach a cut-off voltage of 0.9 volts. According to the present invention, it is preferred that the expanded graphite have a tap density value in the range of 0.09 to 0.14 g/cc.

- 20 The expanded graphite particles of the present invention are purified to a high purity level. The following table lists the desired maximum amount of impurities in parts-per-million (PPM) for each impurity that may be present in the expanded graphite particles:

	<u>TOTAL IMPURITIES</u>	<u>MAXIMUM LIMITS (PPM)</u>
5	a) Antimony (Sb)*	2.0
	b) Arsenic (As)*	1.0
	c) Molybdenum (Mo)*	2.0
10	d) Vanadium (V)*	10.0
	e) Chromium (Cr)*	5.0
15	f) Iron (Fe)*	150.0
	g) Copper (Cu)*	5.0
	h) Tin (Sn)*	2.0
20	i) Aluminium (Al)	25.0
	j) Calcium (Ca)	75.0
25	k) Cobalt (Co)	3.0
	l) Lead (Pb)	5.0
	m) Nickel (Ni)	5.0
30	n) Silicon (Si)	200.0

Accordingly, the preferred expanded graphite realises an aggregate total maximum limit of no more than 490 ppm of impurities, amounting to 0.049% impurities or 99.951% pure expanded graphite. It is preferred that the expanded graphite particles have a purity of at least 99.95% or higher. The impurities deemed most critical are marked with an (*) and include antimony, arsenic, molybdenum, vanadium, chromium, iron, copper, and tin, which together should preferably have an aggregate total maximum allowed amount of no more than 170 ppm of critical impurities, amounting to 0.017% critical impurities or 99.983% non-critical impurities.

To optimise service performance, it is preferred that the expanded graphite particles have a kerosene absorption value in the range of 2.2 to 3.5 millilitres per gram (ml/g), more preferably 2.7 to 3.1 millilitres per gram. Further, it is also preferred that the expanded graphite have both an average particle size in the range of 17 to 32 μm and a d_{90} value in the range of 40 to 85 micrometers, and yet more preferred that the expanded graphite also have an average surface area-to-mass ratio of greater than or equal to 18 m^2/gram . The most preferred particle size distribution of the expanded graphite is defined by an average particle size of 17 to 32 micrometers, a d_{90} value of 40 to 85 μm and a d_{10} value of 3-9 micrometers. It is preferred that the tap density have a preferred value in the range of 0.09 to 0.14 g/cc. It is further preferred that the expanded graphite have a Scott density no greater than 0.07 grams/millilitre (g/ml), and preferably no greater than 0.05 g/ml.

According to a second embodiment, a non-acid treated, de-laminated graphite may be used in place of the acid-soaked, thermally treated, expanded graphite described above. The non-acid treated, de-laminated graphite is processed in a thermal treatment process, but does not require the use of acid soaking. Instead, a natural graphite is placed in an oven and heat treated as explained above, but without the acid soaking treatment. The non-acid, thermal treatment process causes the natural graphite to de-laminate to form multiple thin graphite strips.

According to yet another embodiment, a chemically treated synthetic expanded graphite can be used. This chemically treated, synthetic expanded graphite can be used in

cathode mix ratios with electrolytic manganese dioxide of 20 : 1 oxide-to-carbon weight ratio. Using flooded half-cell testing, the synthetic expanded graphite exhibits a high-rate performance at 50 mA/g manganese dioxide constant current. Cathode mixes containing this synthetic, chemically treated expanded graphite have also shown low cathode pellet resistivities with values in the range of cathode mixes containing a thermally prepared expanded graphite as explained above.

Based on initial test results, standard AA-size cells containing this specific synthetic expanded graphite in the cathode exhibit high-rate service performance greater than current factory products, as this material provides increased cathodic service performance in both ring-moulded and impact-moulded cathode assemblies.

Referring to Figure 11, a method 60 is provided for determining an optimum expanded graphite from numerous samples for use in the cathode 20 of the electrochemical cell 10. The method includes sampling one graphite at a time, from a plurality of graphite samples, such as graphite Sample A 62, Sample B 64, and Sample C 66, as shown. Each sample of graphite may include natural graphite obtained from a mine and purified in a purity process. Graphite obtained from different mines and purified by different processes may produce differing characteristics which, in turn, may affect the characteristics of an expanded graphite produced therefrom. Given a sample of graphite, methodology 60 includes the step 68 of producing an expanded graphite. The expanded graphite may be produced according to the above-described method 40, as set forth in Figure 2, which includes acid treatment, heating, and milling to achieve a particular particle size, shape, and other characteristics.

With the expanded graphite produced, step 70 of method 60 measures various characteristics of the produced expanded graphite particles. Measurements include measuring the average particle size of the expanded graphite, such as the d_{50} , d_{90} and d_{10} average particle size measurements, as taken with a Microtrac measuring device. Another
5 measuring characteristic includes measuring the surface area of the expanded graphite particles, preferably taken as an average surface area. The bulk density, as well as real density, of the expanded graphite is also measured. Density is measured in grams per cubic inch, and may include a Scott volume. The measurement characteristics further include measuring the kerosene absorption for the expanded graphite, as well as tap
10 density. It should be appreciated that other characteristics of the expanded graphite may likewise be measured and used in accordance with method 60.

Based on the aforementioned measured characteristics, measured data curves can be produced from which the performance for a given expanded graphite may be calculated
15 in step 72. Measured data curves may be similar to the graphs shown in Figures 5-10. Based on the calculated performance for the measured expanded graphite, in step 74 a determination is made as to the optimum expanded graphite for use in the cathode 20 of cell 10 by comparing the calculated performance for various expanded graphites. For a given expanded graphite, the performance calculation may be used to adjust feedback set
20 points, as set forth in block 76, which may be used in the production of the expanded graphite.

Set point adjustments may include manual or automatic process control adjustments, such as adjusting the soaking time for acid treatment of the graphite,

adjusting the time and temperature for heat treatment, and adjusting the milling speed and time used to obtain a particular expanded graphite average particle size. According to method 60, the calculated performance could be used to adjust the process of producing expanded graphite for a particular sample of graphite. Also, various samples of graphite
5 may be used to produce the expanded graphite, and the performance characteristics can be measured and compared to determine the optimum expanded graphite from the available samples.

Claims:

1. An electrochemical cell comprising a positive electrode having an active material and an electrically conductive carbon material including expanded graphite particles,
5 characterised in that the expanded carbon particles have a kerosene absorption value in the range of 2.2 to 3.5 ml/g.
2. An electrochemical cell according to claim 1, wherein the expanded graphite particles have an average particle size in the range of 17 to 32 μ m.
- 10 3. An electrochemical cell according to claim 1 or 2, wherein the expanded graphite particles have a d_{90} value in the range of 40 to 85 μ m.
4. An electrochemical cell according to any preceding claim, wherein the expanded
15 graphite particles have a d_{10} value in the range of 3 to 9 μ m.
5. An electrochemical cell according to any preceding claim, wherein the expanded graphite particles have a kerosene absorption in the range of 2.7 to 3.1 ml/g.
- 20 6. An electrochemical cell according to any preceding claim, wherein the expanded graphite particles have a surface area-to-mass ratio of at least 18 m²/g.
7. An electrochemical cell according to any preceding claim, wherein the expanded graphite particles have a tap density in the range of 0.09 to 0.14 g/cc.

8. An electrochemical cell according to any preceding claim, wherein the expanded graphite particles have a Scott density of no greater than 0.07 g/ml.

5 9. An electrochemical cell according to any preceding claim, wherein the active material of the positive electrode comprises primarily manganese dioxide.

10. An electrochemical cell according to any preceding claim, wherein the expanded graphite particles are derived from natural graphite.

10

11. An electrochemical cell according to any preceding claim, wherein the expanded graphite particles comprise 3.2 to 6.25 weight percent of the cathode.

12. An electrochemical cell comprising a positive electrode having an active material
15 and an electroconductive carbon material including expanded graphite particles having a purity level of greater than 99.9 percent, as determined by weight loss on ignition.

13. An electrochemical cell according to claim 12, wherein the graphite particles have a purity level greater than 99.95%

20

14. An electrochemical cell according to any preceding claim, wherein the expanded graphite particles have impurities including any of antimony, arsenic, molybdenum, vanadium, chromium, iron, copper, and tin, and wherein an aggregate total of the impurities amounts to no greater than 200 parts per million.

15. An electrochemical cell according to any of claims 12 to 14 and being as defined in any of claims 1 to 11.

5 16. Graphite as defined in any preceding claim.

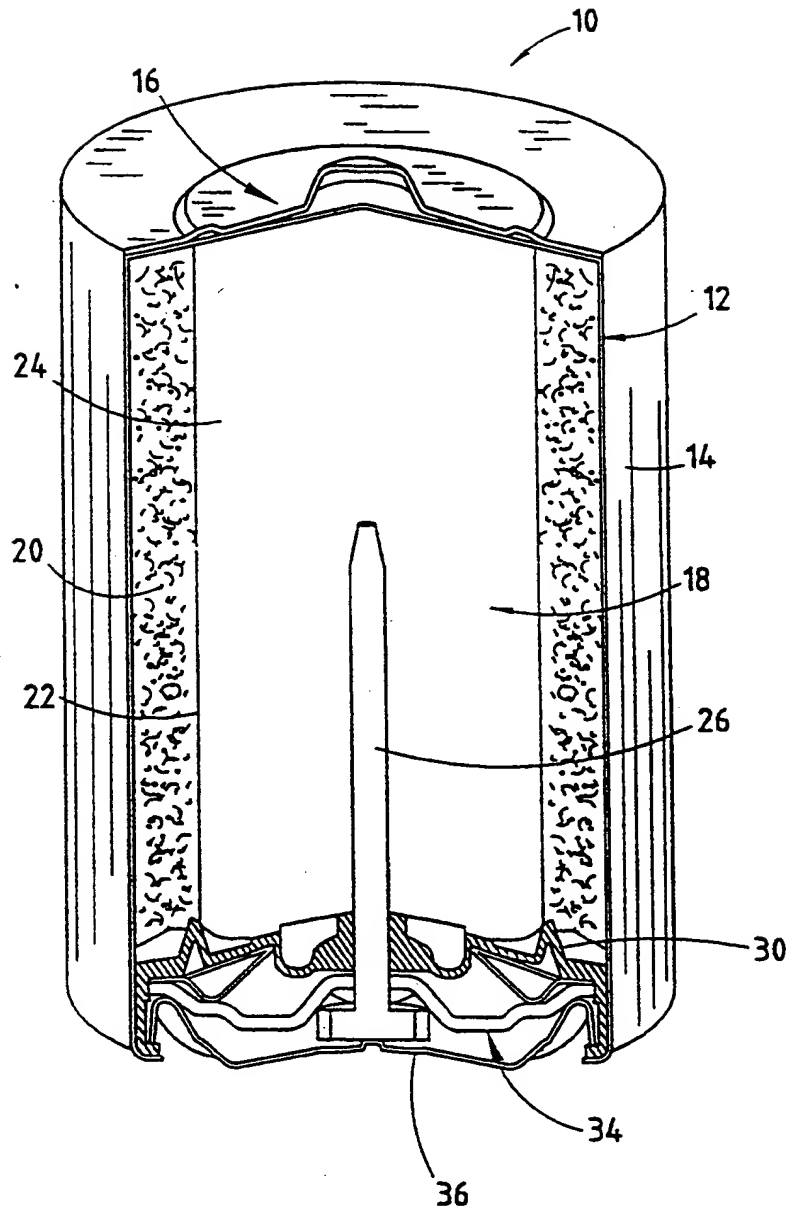


FIG. 1

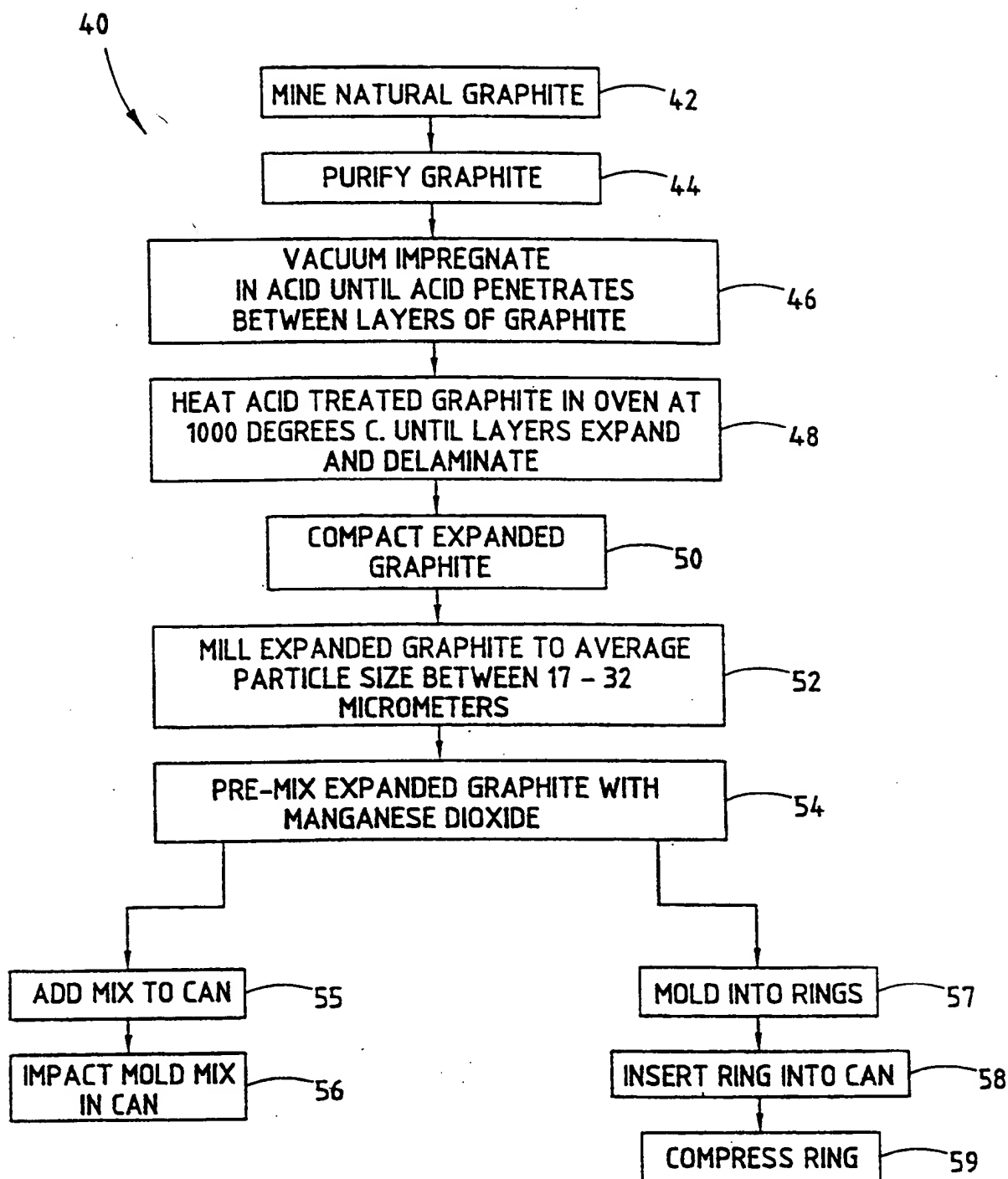


FIG. 2



FIG. 3

PERFORMANCE ANALYSIS

Expanded Graphite	Service* to 0.9V	Microtrac Particle Size (µm)				BET Surface Area	Kerosene Abs.	Pellet Resist. @	%Water (110°C)	Scott Density	Real Density	Surface Area (calc.)	Bulk Volume	Tap Density
		d ₁₀	d ₅₀	d ₉₀	ma*									
S1	97.1	4.96	19.61	43.18	27.51	26.7	2.74	1.78	0.16	0.04	2.30	0.450	0.031	0.11
S2	90.6	4.26	16.51	48.27	29.88	18.1	2.06	1.19	0.12	0.06	2.28	0.492	0.043	0.14
S3	86.9	3.66	15.36	43.35	25.70	19.9	1.94	1.35	0.13	0.05	2.27	0.553	0.046	0.15
S4	66.0	3.13	9.23	15.50	10.31	9.6	1.36	3.44	0.03	0.07	2.26	0.776	0.069	0.22
S5	51.7	5.84	19.51	36.71	23.67	5.7	1.44	6.17	0.05	0.11	2.25	0.372	1.105	0.28
S6	65.2	3.37	10.42	16.36	11.59	8.2	1.37	4.16	0.05	0.07	2.27	0.672	0.068	
S7	77.0	20.69	81.60	160.21	110.02	21.3	4.39	1.61		0.06	2.25	0.139	0.034	0.10
S8	93.0	6.53	21.33	58.07	31.74	23.1	3.51	0.84		0.04	2.30	0.403	0.034	0.11
S9	90.0	4.72	20.42	16.62	44.25	21.5	2.78	1.08		0.05	2.27	0.441	0.042	0.12
S10	72.3	4.72	9.93	18.18	11.05	8.4	1.25	4.37	0.06	0.08	2.25	0.730		0.23
S11	71.9	9.74	19.89	41.93	24.11	4.5	1.35	7.99	0.10	0.11	2.25	0.356		0.28
S12	82.7	10.91	35.06	118.67	54.92	13.7	2.60	1.47	0.10	0.10	2.24	0.258	0.057	
S13	93.1	7.48	23.65	73.09	35.2	22.4	2.77	0.76	0.09	0.10	2.25	0.377	0.035	0.11
S14	77.0	8.99	29.64	82.39	40.8	18.4	3.52	1.33	0.08	0.05	2.28	0.313	0.039	0.12
S15	86.0	8.98	28.80	77.24	37.95	20.0	3.47	1.14	0.08	0.05	2.27	0.318	0.038	
S16	85.0	9.04	29.96	85.26	41.76	18.4	3.20	1.35	0.01	0.05	2.27	0.310	0.039	
S17	76.0	8.99	34.48	94.09	46.43	18.3	4.38	1.56	0.11	0.06	2.29	0.270		0.11

@ with 20:1 O:C ratio, fully relaxed

*ma=mean diameter of area

♦mv=mean diameter of volume

with 20:1 O:C ratio, 100 mA/g EMD

FIG. 4

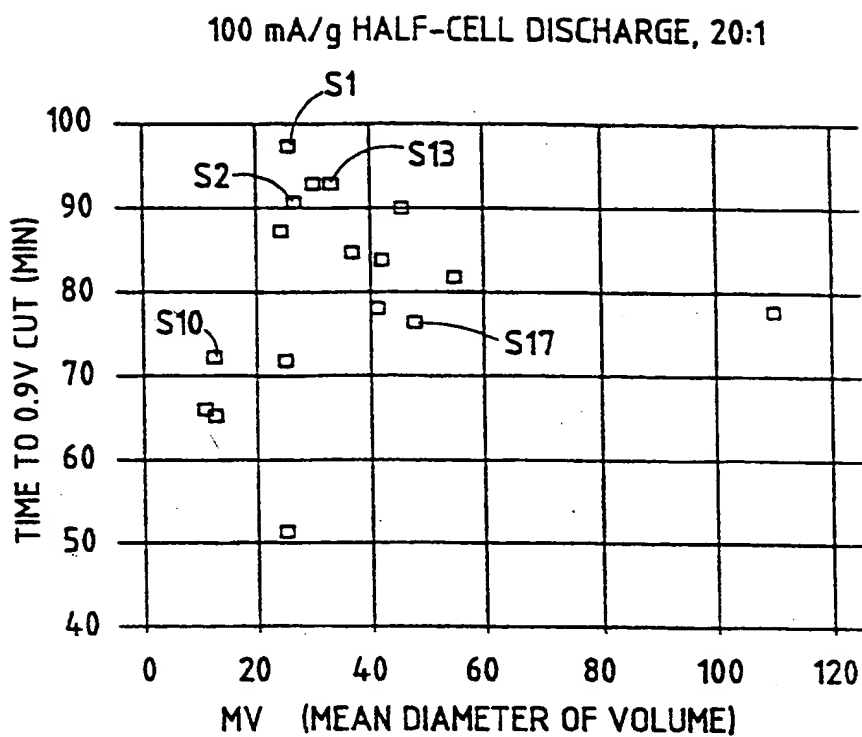


FIG. 5

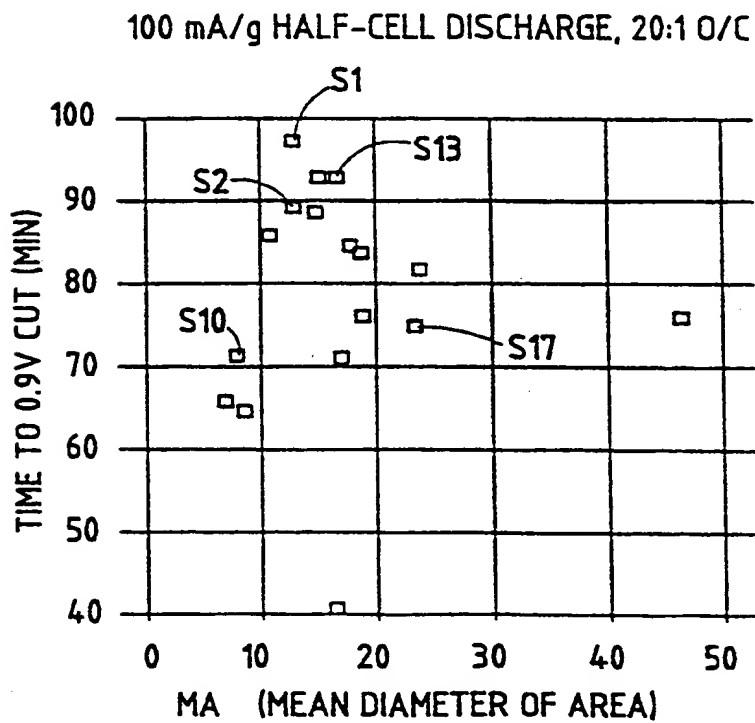
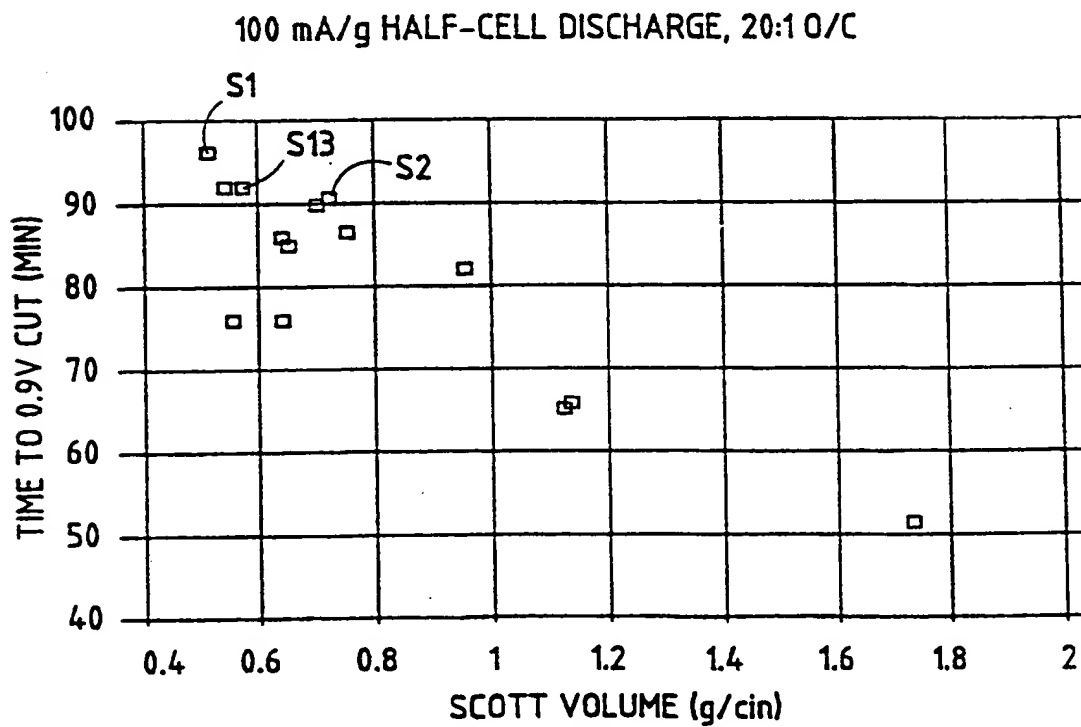
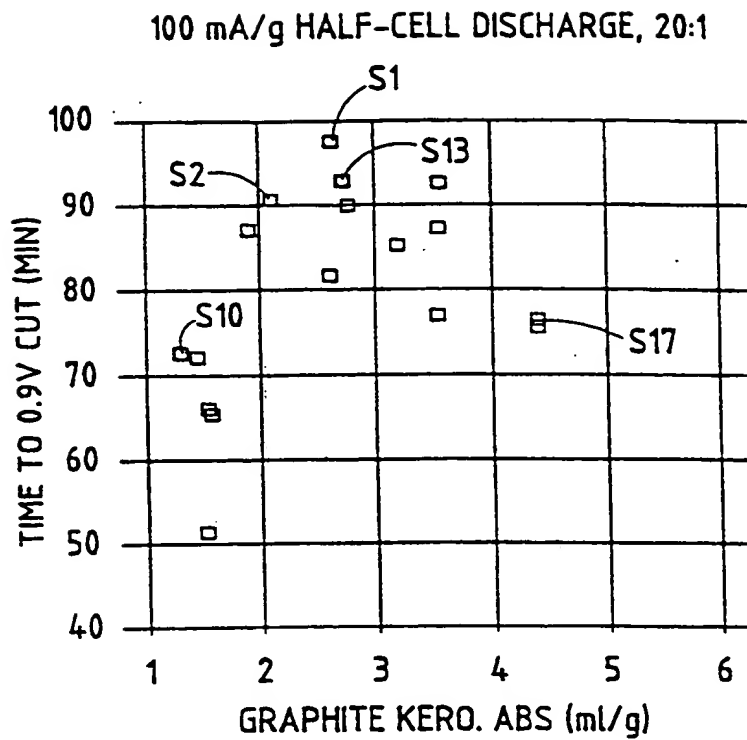


FIG. 6



100 mA/g HALF-CELL DISCHARGE, 20:1

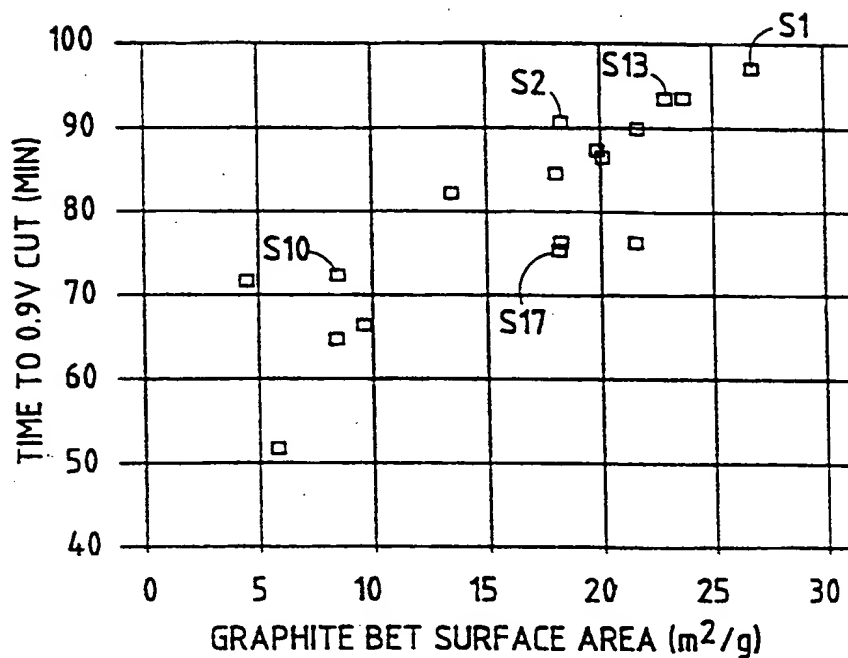


FIG. 9

100 mA/g HALF-CELL DISCHARGE, 20:1 FULLY RELAXED

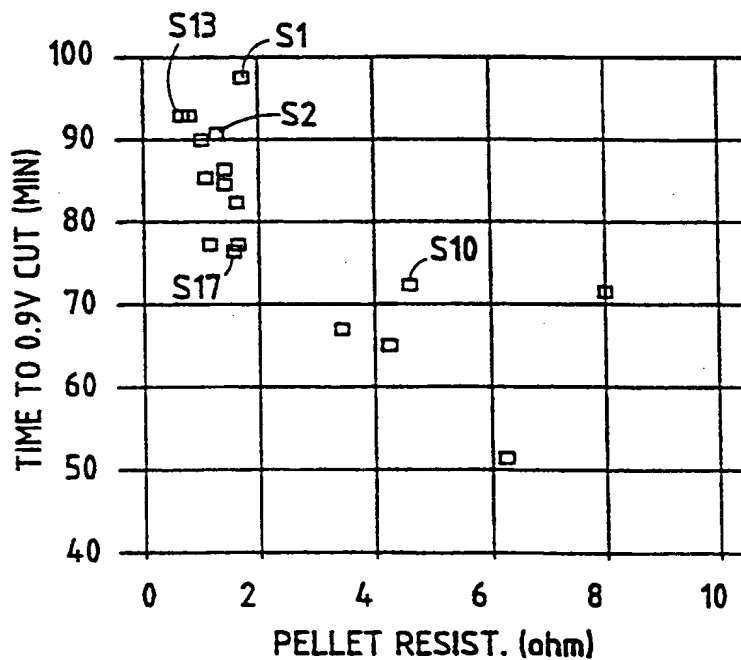


FIG. 10

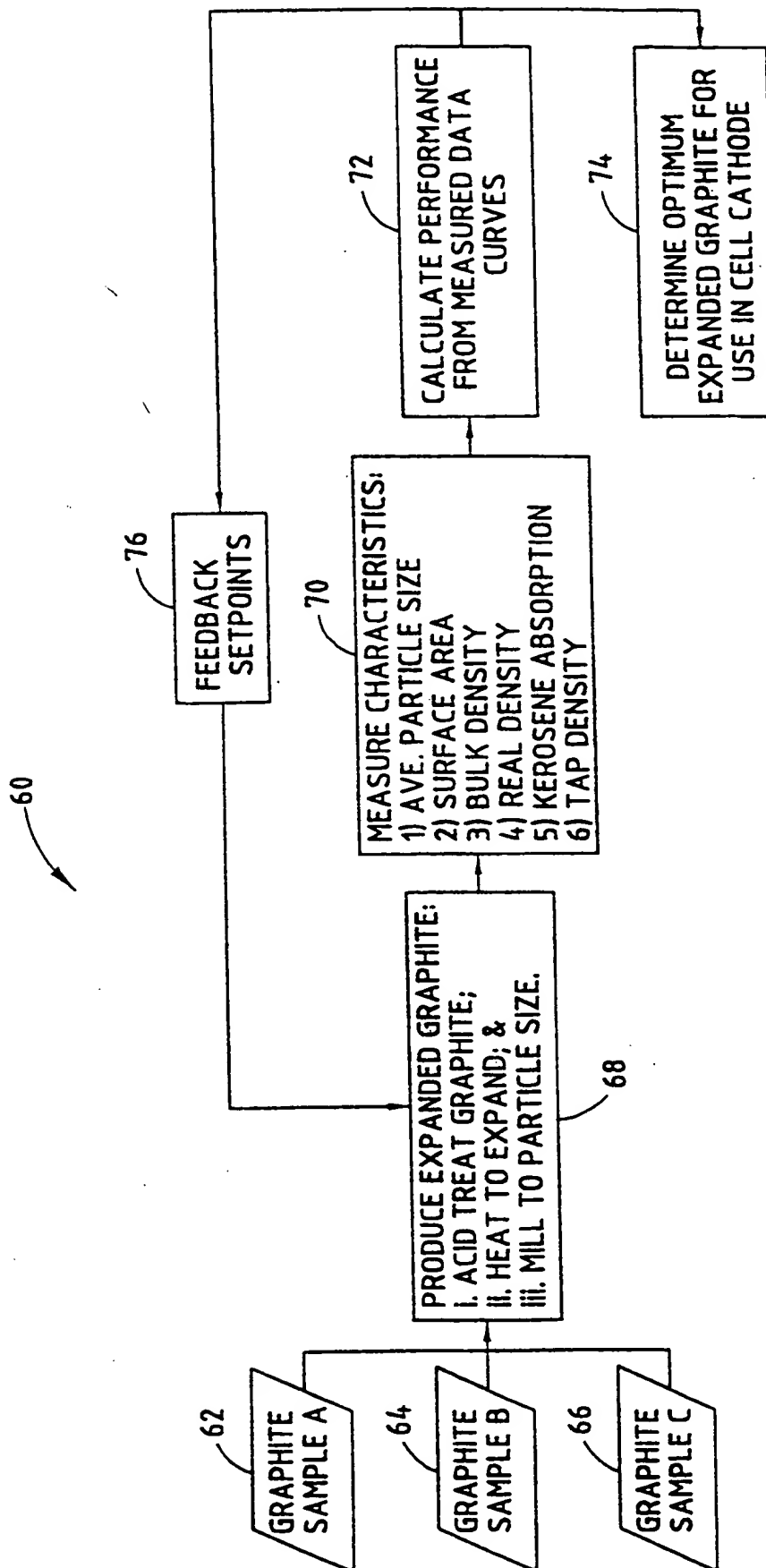


FIG. 11

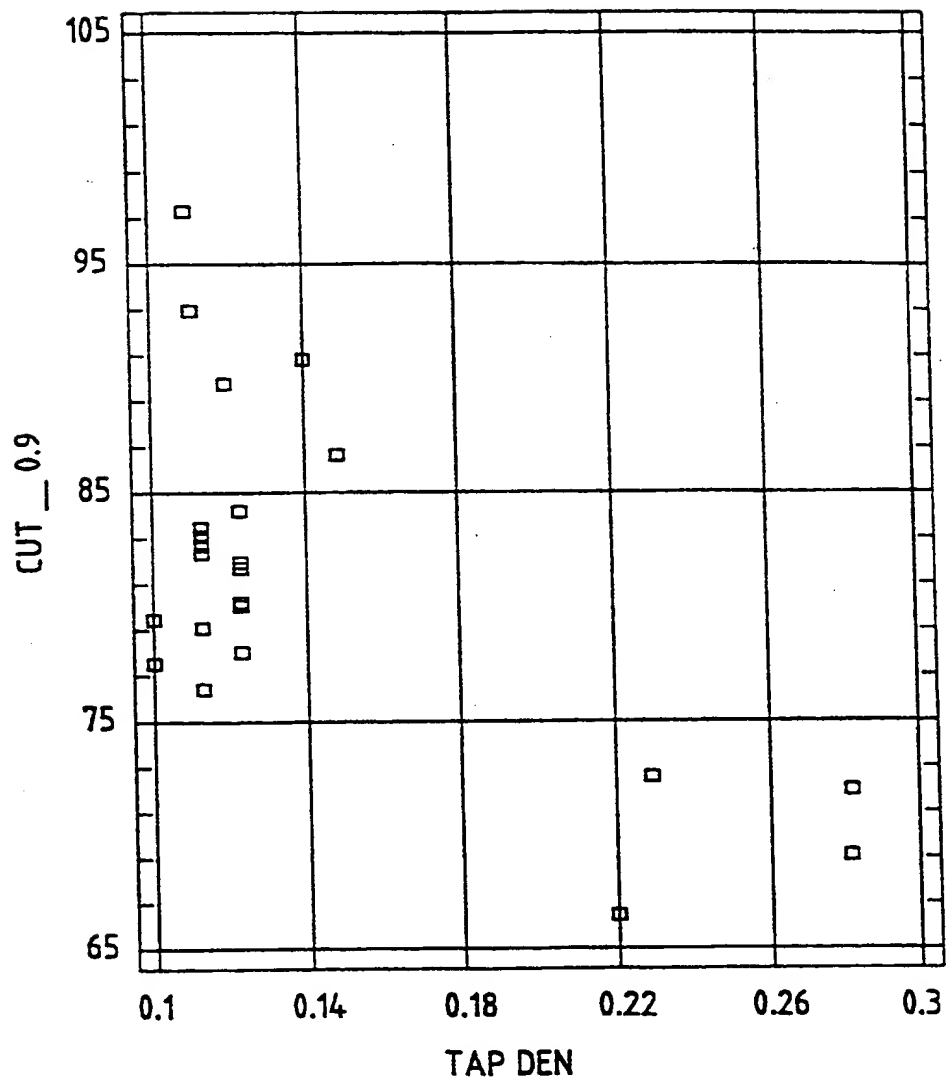


FIG. 12

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 H01M4/62 C01B31/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01M C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 482 798 A (MOTOTANI YUJI ET AL) 9 January 1996 cited in the application see column 1, line 56 - line 67 see column 3, line 6 - line 23 & EP 0 675 556 A (MATSUSHITA ELECTRONIC IND CO LTD) 4 October 1995	1,9,11
A	PATENT ABSTRACTS OF JAPAN vol. 096, no. 010, 31 October 1996 & JP 08 167413 A (MATSUSHITA ELECTRIC IND CO LTD), 25 June 1996 see abstract -/-	1,2

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

19 May 1999

Date of mailing of the international search report

28/05/1999

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Authorized officer

Gamez, A

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 097, no. 009, 30 September 1997 & JP 09 129239 A (MATSUSHITA ELECTRIC IND CO LTD), 16 May 1997 see abstract	1,9,11
A	PATENT ABSTRACTS OF JAPAN vol. 006, no. 006 (E-089), 14 January 1982 & JP 56 128578 A (HITACHI MAXELL LTD), 8 October 1981 see abstract -& DATABASE WPI Section Ch, Week 8147 Derwent Publications Ltd., London, GB; Class L03, AN 81-86009d XP002102849 & JP 56 128578 A (HITACHI MAXELL KK) , 8 October 1981 see abstract	1,9,11
A	EP 0 170 411 A (UNION CARBIDE CORP) 5 February 1986 see page 2, line 9 - line 14 see page 3, line 1 - line 20 see table 1 see claims 1,2	10-12,15
A	PATENT ABSTRACTS OF JAPAN vol. 005, no. 181 (E-083), 20 November 1981 & JP 56 109460 A (JAPAN STORAGE BATTERY CO LTD), 29 August 1981 see abstract -& DATABASE WPI Section Ch, Week 8141 Derwent Publications Ltd., London, GB; Class L03, AN 81-74912d XP002102850 & JP 56 109460 A (JAPAN STORAGE BATTERY CO LTD) see abstract	10
P,A	PATENT ABSTRACTS OF JAPAN vol. 098, no. 012, 31 October 1998 & JP 10 188993 A (RICOH CO LTD), 21 July 1998 see abstract	1,2,6,9, 11
P,A	PATENT ABSTRACTS OF JAPAN vol. 099, no. 001, 29 January 1999 & JP 10 284056 A (SEIKO INSTR INC), 23 October 1998 see abstract	1,2,6

-/--

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	PATENT ABSTRACTS OF JAPAN vol. 098, no. 014, 31 December 1998 & JP 10 245491 A (OSAKA PREFECTURE;NIPPON KARU KK), 14 September 1998 see abstract —	16
A	EP 0 596 801 A (ENVIRONMENTAL SYSTEMS LTD) 11 May 1994 see page 2, line 44 - line 50 see page 3, line 2 - line 5 see page 3, line 39 - line 41 see examples 1-3 —	16
A	EP 0 435 766 A (TECHNION RES & DEV FOUNDATION ;MARYASIN ILYA (IL); SHELEF GEDALIAH) 3 July 1991 see column 2, line 41 - line 55 see column 4, line 24 - line 37 —	16
A	PATENT ABSTRACTS OF JAPAN vol. 009, no. 271 (C-311), 29 October 1985 & JP 60 118618 A (NIHON PIRAA KOGYO KK), 26 June 1985 see abstract —	16

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5482798	A	09-01-1996	JP 7272715 A	20-10-1995
			AU 670897 B	01-08-1996
			AU 1493695 A	02-11-1995
			CA 2145564 A,C	29-09-1995
			CN 1115122 A	17-01-1996
			EP 0675556 A	04-10-1995
			SG 28238 A	01-04-1996
EP 0170411	A	05-02-1986	JP 61107663 A	26-05-1986
EP 0596801	A	11-05-1994	IL 103641 A	14-11-1996
			DE 69318375 D	10-06-1998
			DE 69318375 T	29-10-1998
			JP 6279011 A	04-10-1994
EP 0435766	A	03-07-1991	AU 6846390 A	27-06-1991
			CA 2032965 A	26-06-1991
			JP 4219307 A	10-08-1992
			US 5282975 A	01-02-1994